Use of ClO2 for removal of estrogenic substances in wastewater

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(54) **Title**: USE OF ClO_2 FOR REMOVAL OF ESTROGENIC SUBSTANCES IN WASTEWATER

(57) **Abstract**: The present invention pertains to wastewater treatment. More particularly, the invention concerns inactivation of biologically active compounds, such as estrogenic compounds, present in wastewater comprising sewage by the use of an oxidant, such as ClO_2. A method is disclosed for inactivating one or more estrogenic substance(s) in wastewater, such as in a wastewater treatment plant, said method comprising a step of adding a dose of ClO_2 to the water to be discharged, and said ClO_2-dose being less than the ClO_2- demand of the water to be discharged.

Use of ClO_2 for removal of estrogenic substances in wastewater

TECHNICAL FIELD OF THE INVENTION

The present invention pertains to wastewater treatment. More particularly, the invention concerns inactivation of biologically active compounds, such as estrogenic compounds, present in wastewater comprising sewage by the use of an oxidant, such as ClO_2.

BACKGROUND OF THE INVENTION

Effluent of conventional waste water treatment plants is known to comprise significant amount of biologically active compounds. These compounds can cause undesired effects in nature, and may also be potentially harmful for humans.

One example of the effect of such biologically active compounds leaving a waste water plant is the group of estrogenic substances. Estrogen has been shown to contribute to e.g. feminization of male fish living in waters polluted by domestic wastewater comprising sewage effluents. Conclusively, “estrogen pollution” is unwanted, and should be prevented.

Ried et al. (2003) discuss the use of ozone as a tool for removal of pharmaceuticals, endocrine disrupters and pathogens.

Huber et al. (2003) studied the effect of ozone treatment of municipal waste water effluents in a pilot-scale plant. Ozone treatment of waste water appears as a suitable solution in well polished effluent, as they report that a dose of 2 g/m3 can remove estrogens and a range of pharmaceuticals and other undesired chemicals.

However, ozone treatment has a high capital cost of installation of k€ 100-300 for a medium sized waste water treatment plant (Joss et al., 2008). The

spatial and technical requirements comprise also provision of a reaction chamber which has to be put into the treatment train, most likely along with some means of destroying excess ozone, such as e.g. carbon filter or UV-treatment. Once installed, the running costs may be reasonable for larger installations, but especially for smaller plants, the costs for treatment per m^3 may be too high for a profitable operation. One reason is e.g. that ozone due to its inherent instability cannot be stored for longer periods (Joss et al., 2007; Ried et al., 2007).

Huber et al. (2005) assessed the potential of ClO_2 for the oxidation of pharmaceuticals during water treatment. The experiments are based on "natural" waters, such as surface water and ground water.

Hoigné & Bader (1994) disclose that oxidation of organic material by ClO_2 is considered to be highly selective with a strong preference for the oxidation to occur initially at few functional groups. For phenolic compounds, the reaction rate depends directly on the relation between the actual pH in the water and the pKa of the phenolic compound.

Chlorine dioxide generators are much simpler than ozone generators and thus have a significantly lower capital cost in the range of k€ 10-30 for a size suitable for e.g. a typical sewage treatment plant. The running cost for ClO_2 production depends e.g. on which reactant chemicals are used, on the marked price from different suppliers, and on the scale of the production. Generally, the running cost of producing ClO_2 for water treatment ranges from about the same to the double of ozone per mass unit, depending on scales of consumption and method of production.

Andersen et al. (2007) has investigated the fate of parabens (methylparaben, ethylparaben, propylparaben, butylparaben, and isobutylparaben) in a greywater reuse system. These parabens are commonly used as

antimicrobial agents in e.g. personal care products, food, pharmaceutical and household products. ClO_2 treatment of the biologically treated effluent with dosages down to 0.75 mg/ml resulted in more than 97% reduction of the parabens investigated. Chemically, parabens are alkyl esters of p-hydroxybenzoic acid, and they posses pKa values in the range of 8.17 – 8.37. It should be noted that the greywater investigated did not comprise sewage effluents, and that other estrogenic compounds, such as Bisphenol A (BP), 17β estradiol (E2), Estrone (E1), 17α ethinylestradiol (EE2) and Nonylphenol (NP) were absent in the extensively biologically treated greywater investigated by Andersen et al. (1997). E1, E2, and EE2 are also called steroid estrogens, and are commonly found in urine and thus in sewage. NP and BPA can e.g. come from detergents, emulisifiers and/or plastics, and again, they have quite different chemical structures compared to parabens.

In conventional sewage, the paraben-related estrogenic effect is minimal compared to the estrogenic effect of e.g. BPA, E2, E1, EE2, and NP (random order). These compounds are chemically different from parabens, and they possess a significantly higher pKa values.

Estradiol (17β-estradiol) is considered to be the major estrogen hormone in humans and most animals. The chemical can e.g. be identified by its CAS registry number 50-28-2. Ethynylestradiol is a derivative of estradiol. Ethynyl estradiol is an orally bio-active estrogen used in almost all modern formulations of combined oral contraceptive pills. It is one of the most commonly used medications.

Parabens - in contrast to E1, EE2, E2, BPA, and NP - are readily degradable during biological degradation, such as during secondary treatment in a water treatment plant, such as a sewage treatment plant, or a water treatment plant treating waste water comprising significant amounts of sewage.

Consequently, the problem of estrogenic water effluents from water treatment plants is predominantly due to one or more of compounds EE2, E2, E1, NP, and BPA (listed in order of falling estrogenicity). This is caused by the paraben-related estrogenic compounds being readily degradable in combination with their significantly lower estrogenic effect or estrogenic potency.

Thus removing parabens alone, either in cosmetics, pharmaceuticals, and/or house hold products, and/or relying on their degradation during e.g. secondary treatment in a (sewage)water treatment plant does not solve the undesired estrogenic effect of the effluent of the outlet of a (sewage)treatment plant, such as on the aquatic fauna, as long as there are significant amounts of other estrogenic substances present, such as one or more of E1, EE2, E2, BPA and/or NP.

The invention provides a novel, surprising, and unexpected method/solution for removal of the estrogenic effect of waste water effluents from a waste water treatment plant, where sewage and/or waste water comprising sewage is treated. Surprisingly and unexpectedly, potent estrogenic compounds which are not readily degradable, such as E1, EE2, E2, BPA and/or NP, are efficiently inactivated upon treatment with an oxidant, such as ClO_2. Said solution is believed to be e.g. one or more of: reliable, sufficient, environmentally friendly, suitable for industrial application, and/or economically sound. Advantages according to the invention are believed to comprise e.g. one or more of: (i) reduction and/or optimization of the amount of a chemical composition required; (ii) reduction and/or optimization in the amount of a chemical composition discharged into the environment; (iii) reduction and/or optimization of the amount of microorganisms discharged into the environment; and/or (iv) reduction of pollution by one or more estrogenic substance(s).

SUMMARY OF THE INVENTION

The current invention provides a method for inactivation of biologically active compounds in waste water, such as estrogenic substances, by the use of oxidants, such as ClO_2. The current invention is not only suitable for e.g. new wastewater treatment facilities, such as sewage treatment plants, but it can also be applied to existing facilities.

In a first aspect, the current invention concerns a method of inactivating one or more estrogenic substance(s) in a wastewater treatment plant, said method comprising a step of adding a dose of ClO_2 to the water to be discharged, and said ClO_2-dose being less than the ClO_2-demand of the water to be discharged.

In a second aspect, the current invention pertains to a method of treating wastewater, said method comprising the steps of:

- determining the ClO_2–demand of a water sample to be discharged;
- adding a dose of ClO_2 to the water to be discharged, said dose being less than ClO_2–demand of the water to be discharged; and
- inactivating one or more estrogenic substance(s) in the water to be discharged.

In a third aspect, the current invention relates to a water treatment plant adapted to removing estrogenic substances according to any one of the preceding aspects and/or embodiments.

SHORT DESCRIPTION OF THE DRAWINGS

Figure 1. Schematic drawing of a typical tertiary sewage treatment plant. The order and types of processes may vary depending on design strategy and the composition of the water to be treated.

Figure 2. Graphic representation of a concentration profile of ClO_2 added to effluent water from two selected sewage treatment plants ("Lundtofte" and "Lynetten").

Figure 3. Graphic representation of the effect of ClO_2 dosis on steroids estrogens. Left: Lundtofte sewage treatment plant effluent; right: Lynetten sewage treatment plant effluent. Averages of 4 determinations for each treatment are shown, and T-bars indicate the standard error.

Figure 4. Graphic representation of the effect of ClO_2 dosis on industrial phenols and parabenes. Left: Lundtofte sewage treatment plant effluent; right: Lynetten sewage treatment plant effluent. Averages of 2 determinations for each treatment are shown, and T-bars indicate the standard error.

Figure 5. Graphic representation of the effect of ClO_2 dosis on sunscreens. top: Lundtofte sewage treatment plant effluent; bottom: Lynetten sewage treatment plant effluent. Averages of 2 determinations for each treatment are shown, and T-bars indicate the standard error.

Figure 6. Graphic representation of the effect of ClO_2-dosis (horizontal axis) on estrogenic potency in the YES assay. Left effluent from Lundtofte sewage treatment plant, right effluent from Lynetten sewage treatment plant. The bars illustrate the concentration factor required to give an estrogen potency of the extracts which is 50 % (EC50) of the maximal for the E2 standard curve for each sample. T-bar indicates 95% confidence interval.

DETAILED DESCRIPTION OF THE INVENTION

Definitions

The terms "about", "around", "approximately", or "~" indicate e.g. the measuring uncertainty commonly experienced in the art, which can be in the order of magnitude of e.g. +/- 1, 2, 5, 10, 20, or even 50%.

The term "comprising" is to be interpreted as specifying the presence of the stated parts, steps, features, or components, but does not exclude the presence of one or more additional parts, steps, features, or components. E.g., a composition comprising a chemical compound may thus comprise additional chemical compounds etc.

The term “chlorine dioxide” and “ClO_2” in the context of the present invention is meant to comprise a chemical composition with the molecular formula ClO_2, and its Chemical Abstract Service (CAS) registry number 10049-04-4. Without being bound by any theory, it is believed that oxidation by chlorine dioxide (i.e. reduction of ClO_2) comprises the following reactions:

(1) $ClO_2 + e^- \rightarrow ClO_2^-$

(2) $ClO_2^- + 4e^- + 4H^+ \rightarrow Cl^- + 2H_2O$

As seen in reaction (2), the chlorite formed may also act as an oxidant, and it may eventually be reduced to chloride.

The term “wastewater” is meant to comprise any water that has been adversely affected in quality by anthropogenic influence. It comprises liquid waste discharged by domestic residences, commercial properties, industry, and/or agriculture and can encompass a wide range of potential contaminants and concentrations. In the most common usage, it refers to the municipal wastewater that contains a broad spectrum of contaminants resulting from the mixing of wastewaters from different sources.

In the context of the present invention, the terms “wastewater comprising sewage” or “wastewater/sewage” can be used interchangeably and are meant to comprise any wastewater comprising significant amounts of sewage.

The term "comprising significant amounts of sewage" is meant to comprise wastewater with measurable/detectable amounts of estrogenic substance(s) derived from sewage. Often, said one or more estrogenic substance will be present above a legal threshold value. Tables I and/or II comprise estrogenic substances commonly found in sewage.

The terms "wastewater treatment plant", abbreviated (WWTP) and "water treatment plant" can be used interchangeably and are meant to comprise a site where water, such as wastewater is processed or treated. Often such treated wastewater is discharge back to the environment. WWTPs may comprise mechanical, chemical and biological treatment systems, including any combination thereof. Wastewater treatment can be grouped into three stages, called *primary*, *secondary* and *tertiary treatment*. An example illustrating e.g. different processes/operations in a wastewater treatment plant is given in Figure 1.

The term "sewage" is meant to comprise any water-carried wastes, in either solution or suspension, that flow away from a community. Also known as wastewater flows, sewage is the used water supply of the community. Depending on their origin, wastewater can be classed as sanitary, commercial, industrial, or surface runoff.

The spent water from residences and institutions, carrying body wastes, washing water, food preparation wastes, laundry wastes, and other waste products of normal living, are classed as domestic or sanitary sewage. Liquid-carried wastes from stores and service establishments serving the immediate community, termed commercial wastes, are included in the sanitary or domestic sewage category if their characteristics are similar to household flows. Wastes that result from an industrial process or the production or manufacture of goods are classed as industrial wastes. Their flows and strengths are usually more varied, intense, and concentrated than

those of sanitary sewage. Surface runoff, also known as storm flow or overland flow, is that portion of precipitation that runs rapidly over the ground surface to a defined channel. Precipitation absorbs gases and particulates from the atmosphere, dissolves and leaches materials from vegetation and soil, suspends matter from the land, washes spills and debris from urban streets and highways, and carries all these pollutants as wastes in its flow to a collection point.

The term “sewage treatment plant” is meant to comprise a site where sewage is processed or treated. Sewage treatment plant may comprise mechanical, chemical and biological treatment systems, including any combination thereof. A system of sewer pipes (sewers) collects sewage and takes it for treatment or disposal. Where a main sewerage system has not been provided, sewage may be collected from homes by pipes into septic tanks or cesspits, where it may be treated or collected in vehicles and taken for treatment or disposal. Properly functioning septic tanks require emptying every 2-5 years depending on the load of the system. Sewage and waste water is also disposed of to rivers, streams.

Greywater, also known as sullage, is non-industrial wastewater generated from domestic processes such as dish washing, laundry and bathing. Greywater comprises 50-80% of residential wastewater. Greywater comprises wastewater generated from all of the house's sanitation equipment except for the septic tank (water from toilets is blackwater, or sewage). Greywater is distinct from blackwater in the amount and composition of its chemical and biological contaminants (from feces, urine and/or toxic chemicals). Greywater gets its name from its cloudy appearance and from its status as being neither fresh (white water from groundwater or potable water), nor heavily polluted (blackwater). According to this definition, wastewater containing significant food residues or high concentrations of

toxic chemicals from household cleaners, etc., may be considered "dark grey" or yucky water.

The term “primary treatment” is meant to comprise one or more processes in a wastewater/sewage treatment plant, wherein said process(es) e.g. comprise one or more of screening and/or removal of larger particles, separation of sand, removal of sand, settling of solids, and/or removal of solids, and/or any combination thereof. Usually, “primary treatment” comprises physical separation of undesired compounds.

The term “secondary treatment” is meant to comprise is one or more processes in a wastewater/sewage treatment plant designed to degrade biological content of the (waste) water/sewage to be treated, such as biological contamination derived from human waste, food waste, soaps and detergent. Many municipal and industrial wastewater treatment plants use one or more aerobic biological processes during “secondary treatment”. “Secondary treatment” comprises usually biological degradation of undesired compounds by the use of microorganisms.

The term “tertiary treatment” is meant to comprise one or more processes in a wastewater/sewage treatment plant, wherein sad process (es) may comprise one or more of nitrification, denitrification, biological phosphor removal, chemical phosphor removal, filtering for reduction/removal of suspended particles, extended settling for reduction/removal of suspended particles, and/or any combination thereof.

“Nitrification” comprises e.g. biological oxidation of ammonia with oxygen into nitrite followed by the oxidation of nitrite into nitrate.

“Denitrification” comprises e.g. a microbial facilitated process of dissimilatory nitrate reduction that may ultimately produce molecular nitrogen (N_2). It is

believed that this may occur through a series of intermediate gaseous nitrogen oxide products. Such a respiratory process reduces oxidized forms of nitrogen in response to the oxidation of an electron donor such as organic matter. The preferred nitrogen electron acceptors are believed to be nitrate (NO_3^-) and nitrite (NO_2^-).

"Chemical phosphor removal" comprises a process of purifying wastewater/sewage comprising phosphate, wherein phosphate is transformed to insoluble salts, such as by addition of trivalent cations, typically iron or aluminium. Said salts are then removed fro the water with excess sludge.

"Biological phosphor removal" comprises a microbial process of purifying wastewater/sewage comprising phosphate, wherein phosphate is assimilation by microorganisms, such as sludge bacteria. The phosphor/phosphate content in such microorganisms may significantly exceed the natural phosphate content.

In the context of the present invention, the term "estrogenic substance" or "estrogenic substances" is meant to comprise a chemical composition, or a group of chemical compositions wherein said substance or chemical can mimic the effect of the natural estrogen hormone (this can also be called "showing or possessing an estrogenic effect").

Without being bound to any theory, it is believed that this may comprise one or more compositions that are able to bind and or interact with an estrogen receptor in a cell and stimulate a response comparable to the estrogen hormone. The group of estrogenic substances may comprise one or more and any combination of "natural" estrogen hormone(s), one or more drug(s)/chemical composition(s) which are purposely made to be identical or similar to estrogens, and any natural and synthetic chemical(s)/chemical

composition(s), which is/are not purposely meant to be estrogenic substances.

According to the invention, an estrogenic substance can also be a chemical compound listed in Table I and/or Table II, or a derivative of said chemical compound. Further examples of one or more estrogenic compound(s) commonly found in wastewater, sewage and/or wastewater comprising sewage are meant to comprise one or more compounds selected from the group comprising parabens, industrial phenols, sun screens, steroid estrogens, phtalates, natural compounds, and pesticides, wherein the group of parabens is meant to comprise e.g. : methyl 4-hydroxybenzoate (MP), CAS 99-76-3; ethyl 4-hydroxybenzoate (EP), CAS 120-47-8; propyl 4-hydroxybenzoate (PP), CAS 94-13-3; isobutyl 4-hydroxybenzoate (isoBP), CAS 4247-02-3; butyl 4-hydroxybenzoate (BP), CAS, 94-26-8; pentylparben, CAS6521-29-5; hexylparaben, CAS 1083-27-8; heptylparaben, CAS 1085-12-7; octylparaben, CAS 1219-38-1; the group of industrial phenols is meant to comprise: bisphenol A (BPA), CAS 80-05-7; nonylphenol (NP), CAS 84852-15-3, 4-tert-octylphenol (OP), CAS 140-66-9; the group of sun screen is meant to comprise: 2-ethylhexyl trans-4-methoxycinnamat (OMC), CAS 83834-59-7; 2-hydroxy-4-methoxybenzophenon (BP-3), CAS 131-57-7; 5-Chloro-2-hydroxybenzophenone (BP-7), CAS 85-19-8; homosalate (HMS), CAS 118-56-9; 2-ethylhexyl 4-(dimethylamino)benzoate (OD-PABA), CAS 21245-02-3; 3-(4'-methylbenzylidene) camphor (4-MBC), CAS 36861-47-9; the group of steroid estrogens is meant to comprise: estrone (E1), CAS 53-16-7; 17β-estradiol (E2), CAS 50-28-2; 17α-ethynyl estradiol (EE2), CAS 57-63-6; 17α-estradiol, CAS 57-91-0; estriol, CAS 50-27-1; mestranol, CAS 72-33-3; 2-hydroxyestrone, CAS 362-06-1; 2-hydroxy-17β-estradiol, CAS 362-05-0; 17β-estradiol 17-(b-D-gluconide), CAS 15087-02-2; estriol 17-(b-D-glucoronide), CAS 7219-89-8; estriol 16α-(β-D-glucuronide), CAS 1852-50-2; the group of phthalates is meant to comprise: benzyl-n-butylphthalate, CAS 85-68-7; di-n-butylphthalate, CAS 84-74-2; di-sec-octyl phthalate, CAS 117-

81-7; the group of natural compounds is meant to comprise: genistein, CAS 446-72-0; b-sitosterol, CAS 83-46-5; zearalenon, CAS 17924-92-4; zearalenol, CAS 36455-72-8; the group of pesticides is meant to comprise: sumithrin, CAS 26002-80-2; fenvalerate, CAS 51630-58-1; d-trans allethrin, CAS 584-79-2; permethrin, CAS 52645-53-1; fenarimol, CAS 60168-88-9; triadimefon, CAS 43121-43-3; triadimenol, CAS 55219-65-3; 1-hydroxychlordene, CAS 2597-11-7; p,p-DDT, CAS 50-29-3; endosulfan, CAS 115-29-7; wherein CAS indicates a compound's Chemical Abstract Service registration number. Without wanting to be bound by any theory, it is believed that derivates of chemical compounds listed above may also possess an estrogenic effect.

The terms "dose" or "dosage" may be used interchangeably and is/are meant to comprise a defined amount of one or more chemical composition(s) added to e.g. water relative to one or more of e.g. volume, weight, time, molar ratio, and any combination thereof, such as e.g. 1 mg/l, 1 g/m^3, 1 g/h, 1 g/h/ m^3. Likewise, "dosing" is meant to comprise the act of adding a dose and/or providing a dosage. Said "dosing" may also comprise adding a chemical composition to a constant or non-constant flow of water, such as e.g. wastewater, sewage and/or wastewater comprising sewage during or after treatment at a wastewater/sewage treatment plant, such as after primary/physical and secondary/biological purification, and before discharge to the environment.

A "controlled dose" may relate to a dose of ClO_2, wherein said dose is e.g. not too low and not too high for removing an estrogenic substance to a satisfactory level, such as below a (defined) threshold level. According to an embodiment of the invention, a controlled dosed can e.g. provide a satisfactory (specific) removal rate, such as comparable or identical to a (specific) removal rate(s) listed below. If a ClO_2-dose is too low, this may indicate that e.g. a removal of one or more estrogenic substance(s) to below

a (defined) threshold level may not occur. If a ClO_2-dose is too high, this may indicate e.g. that more ClO_2, or significantly more ClO_2, (e.g. ~1.5; ~2.0; ~2.5; 3.0; 3.5; 4.0; 4.5; 5.0 × or more) is used than required to remove one or more estrogenic substance(s) to below a (defined) threshold level. A ClO_2-dose can also be to high, when the ClO_2-dose is greater than the ClO_2-demand. According to an embodiment of the invention, it is undesirable to add more or significantly more ClO_2-dose than required to remove one or more estrogenic substance(s) to below a (defined) threshold level. A controlled dose can be delivered to a flow of water in which the volume of water, the concentration of estrogenic chemicals and/or the concentration of compounds which reacts with and consumes ClO_2, varies with time by automatically adjusting the amount of chemical added based on measuring/assessment/prediction of e.g. one or more of the parameters oxidant/ClO_2-demand, concentration of one or more estrogenic chemicals, concentration of reactive organic matter, etc., and any combination thereof.

The term “oxidant demand” is meant to comprise the amount of an oxidant consumed within a defined measure of time by reaction with any material, chemical composition(s) and/or compound(s), including any reactive organic matter, microorganisms, algae etc. present in the water sample, e.g. a sample of treated wastewater comprising sewage after primary and/or secondary treatment.

Accordingly, the term “ClO_2-demand” is meant to comprise the amount of ClO_2 consumed within a defined measure of time by reaction with any material, chemical composition(s) and/or compound(s) including reactive organic matter, occurring in water, such as e.g. treated wastewater comprising sewage e.g. after primary and/or secondary treatment.

“Oxidant demand” or “ClO_2-demand” can also mean to comprise the amount of an oxidant such as ClO_2 sufficient/required to inactivate the estrogenic

compounds within a defined period of time by reaction with one or more chemical compositions and/or compounds, including reactive organic matter, occurring in water, such as e.g. wastewater, including treated sewage. "Oxidant demand" or "ClO_2-demand" may be measured/assessed by experimentation for example by measuring the consumption of ClO_2 after it has been added, by measuring the concentration of estrogenic substances and estimating the amount of oxidant required, by measuring the specific removal rate (se later) of a estrogenic compound in the waste water, by measuring the reduction of ClO_2 to Cl^- and/or Cl_2 for example by measuring the production of Cl_2 or measured by any combination of the above.

The "oxidant demand" can also be defined as the consumed ClO_2 as determined by measuring the concentration of ClO_2 in a defined volume of a water sample four hours after 25 mg ClO_2 per litre were added, while the water sample has been kept at ambient temperature and without light.

The terms "(any) material" or "(any) endogenous material", which can be used interchangeably, is meant to comprise one or more compound, gas, liquid, chemical composition, etc., including pharmaceutical, drug, cosmetic, dissolved, dispersed and/or suspended, including any combination thereof, comprised in (waste)water to be treated or treated according to the present invention. Commonly, this may include any "non-water material" present in wastewater, sewage, and/or wastewater comprising sewage before, during or after treatment in a wastewater/sewage treatment plant.

In the context of the invention, the term "reaction time" is meant to comprise the time from addition of a chemical composition, such as addition of ClO_2, until the time point of sampling and/or measuring the remaining concentration.

The term "threshold (limit) level" is meant to comprise a defined concentration of a chemical composition, such as a harmful or potentially harmful substance or chemical composition. This may also comprise the highest/maximum concentration allowed by an authority or legal standard for water released into the environment in order to protect e.g. humans, animals, or nature from a (potentially) harmful effect. A relevant authority may also decide a concentration limit for an estrogenic chemical which is permitted to be released. This may be a concentration of an individual chemical or an effective concentration, such as the sum of concentrations of different estrogenic chemicals. A weighting may be applied to compensate for the different estrogenic potency of different chemicals/chemical compositions. The latter may be measured directly with a biological assay using an estrogen dependant endpoint or be calculated from concentrations of chemicals which are measured individually by chemical methods.

The term "estrogen-related biological effect" is meant to comprise a change in the condition of a subject, such as a human, animal, mammal, vertebrate, insect, plant, yeast, fungus, bacterium, or any part of said subject, including one or more cells, cell-lines, and/or cell cultures, including any combination thereof, wherein said change is caused and/or mediated comprising the estrogen receptor system. Such a change may be in a value of a concentration of a molecule or the production of an enzyme.

The term "detection level of a biological assay" is meant to comprise the minimal concentration of a chemical composition which is able to produce a response which is statistical distinguishable from e.g. a negative control, not comprising said chemical composition.

The term "specific removal rate" is meant to comprise the removal rate of a specific compound, chemical composition, drug, etc., including an estrogenic response concentration equivalent. Such a specific removal rate may be

defined as the difference in concentration before (C_0) and concentration after treatment (C_1), divided by the concentration after treatment.
This ratio (r) is a dimensionless number, $r = (C_0-C_1)/C_0$, often expressed as a percentage ($r_{\%}$), wherein $r_{\%} = r \times 100$.

In the context of the invention, and without wanted to be bound by any theory, the term "estrogenic response concentration equivalent" is meant to comprise the following: If e.g. several estrogenic substances are present in water the potential for an effect caused by any estrogenic mechanism(s) to e.g. an organism in the water can be expresses as an effective concentration which is the sum of concentrations of different estrogenic substances. In such a case a weighting may be applied to compensate for the different estrogenic potency/strength of the estrogenic compositions. Such a potency may be calculated, assessed or derived from determining the concentration of each estrogenic composition - which may be measured individually by similar or different chemical methods - if the weighting factors have been determined by experiments with the individual estrogenic composition relative to the natural estrogenic hormone, 17β-estradiol. Alternatively, it can e.g. also be measured directly with a biological assay using an estrogen dependant parameter which can be quantified and the response is related to a standard curve which by convention is obtained by exposing the assay to different concentrations of e.g. the natural estrogenic hormone 17β-estradiol. Both methods of obtaining the equivalent concentration can be related to a concentration of e.g. 17β-estradiol which will induce the same magnitude of estrogenic response and therefore the estrogenic response concentration equivalent may be given a concentration unit e.g. ng/L.

The term "disinfecting" comprises the act or process of reduction of the number of microorganisms.

In the context of the present invention, the term “inactivation” is meant to comprise the oxidation of a compound. In the case of an estrogenic compound or substance, this comprises rendering said compound biological inactive and thereby decreasing its estrogenic effect.

The term “feedback system” or “feedback means” is meant to comprise a system or device arranged or adapted to automatically adjust a dose of one or more chemical compositions to e.g. water based on an output, such as a change in composition/concentration of the water to be treated according to the invention. Accordingly, the dose of ClO_2 provided to the water will change if the content of one or more estrogenic substances changes, whereby the dose will increase if the concentration of estrogenic chemicals increases. According to the invention, ClO_2 can be provided by ClO_2 providing means, said means comprising e.g. comprise a pump connected to a storage tank with a stock solution of ClO_2 or a reactor there ClO_2 is synthesized continuously or batch-wise by reaction between other chemicals (e.g. chlorite and an oxidant, chlorite and an acid, chlorate and an acid and hydrogen peroxide) or electrochemical oxidation of a precursor.

It is believed that a person skilled in the art will not expect or foresee that estrogenic compounds such as E2, EE2, E2, BPA og NP, i.e. estrogenic compounds that are significantly less reactive than parabens and estrogenic compounds that possess significantly higher pKa values than parabens would be readily degradable /inactivated by ClO_2 according to the present invention.

It is believed that the rapid, ClO_2–mediated degradation of parabens occurs via the phenolate ion, while uncharged phenols react significantly slower (Hoigné & Bader, 1994). E1, EE2, E2, BPA and NP possess markedly higher pKa values than e.g. parabens, i.e. >~10.1 versus ~8.1, respectively. Consequently, the phenolate form of any one of E1, EE2, E2, BPA and NP

will be present in an amount 100 lower compared to the phenolate form of a parabens, resulting in a 100 × lower reactivity of E1, EE2, E2, BPA and/or NP.

The biologically treated greywater from which parabens were readily removed by ClO_2 as described by Andersen et al. (1997) had a pH of 8.3 ± 0.1. This implies that close to 50 % of the parabens were present in the deprotonated and reactive phenolate form which is believed to react with ClO_2. In comparison to the greywater investigated, treated wastewater comprising sewage from wastewater treatment plants usually possesses pH values that are lower, such as pH 6.0 to 8.0; the pH of fully treated effluents is often between pH 7.0 and 7.5.

Thus taking pKa of the major and/or predominant estrogenic compound(s) into account, such as the estrogenic steroids and BPA and NP, in combination with the pH of the wastewater, it is believed that only 0.1% of the predominant estrogenic compounds are present in the reactive deprotonated phenolate form in wastewater comprising sewage, such as communal wastewater, for examples wastewater from “Lynetten” and “Lundtofte” (see experimental section), suggesting that a ClO_2-mediated oxidation/inactivation will occur slowly and inefficiently.

In a first aspect, a method is provided, said method providing inactivation of one or more estrogenic substance(s) in a wastewater treatment plant, said method comprising a step of adding a dose of ClO_2 to the water to be discharged, and said ClO_2-dose being less than the ClO_2-demand of the water to be discharged.

In a second aspect, a method of treating wastewater is provided comprising the steps of:

- determining the ClO_2–demand of a water sample to be discharged;

- adding a dose of ClO_2 to the water to be discharged, said dose being less than ClO_2–demand of the water to be discharged; and
- inactivating one or more estrogenic substance(s) in the water to be discharged.

In the following, further embodiments and examples concerning the first and second aspects are presented. These embodiments can be combined, and any combination of any embodiment is to be construed as disclosed in the present description. Often, these embodiments provide additional examples and/or options than presented in the claims.

According to an embodiment of the invention, inactivation of said estrogenic substance(s) occurs within less than 2 minutes, or less than 1 minute after addition of the ClO_2-dose.

According to an embodiment, the ClO_2-demand is the amount of ClO_2 which is consumed when added to a defined volume of said treated water to be discharged within a defined reaction time, such as 0.5 or 1 litre, and 1, 2, 4, or 6 hour. Apart from the definitions presented herein, an example of a determination of a ClO_2-demand is given in the experimental section.

According to an embodiment, the ClO_2-dose or amount of ClO_2 is sufficient to completely eliminate an estrogenic effect of the discharged water (effluent), or to remove the estrogenic effect of the effluent to below a defined threshold level. The estrogenic effect can also be reduced to the detection level, or to a level where the estrogenic effect is no longer considered harmful.

According to an embodiment, the ClO_2-dose is 70%, 50%, or less than 50% of said ClO_2-demand. E.g. depending on the level of estrogenic substances, and/or in combination with further compounds and/or materials present in the sample, the ClO_2-dose can also be higher, such as 75%, 80%, 85%, 90% or

95%, or lower, such as 65%, 60%, 55%, 50%, 45%, 40%, 35% 30%, 25%, 20% or lower.

According to an embodiment of the invention the estrogenic compounds found in wastewater/sewage and inactivated by ClO_2 according to the invention comprise estrogenic compounds which have a pK_a greater than 8.5, 9.0, 9.25, 9.5, 9.75, 10.0, 10.1, or higher. According to an embodiment, the pK_a value of said estrogenic substance(s) is greater than 9.0, 9.5, or 10.0. According to another embodiment of the invention, the pKa value of the estrogenic compound exceeds the pKa value of a paraben (e.g. selected from methyl-, ethyl-, propyl-, butyl-, and/or iso-butyl paraben) by at least + 1.0; + 1.25; + 1.5; + 1.75; + 2.0, or > more than + 2.0.

According to an embodiment, the estrogenic substance(s) is/are selected from the group consisting of one or more of estrogenic stereoid(s), 17β estradiol, Estron, 17α ethynylestradiol, Bisphenol A, and Nonylphenol, including any estrogenic derivative(s) and combination(s) thereof. According to another embodiment of the invention the estrogenic compounds found in sewage and/or wastewater comprising sewage comprise one or more compounds selected from the group comprising Bisphenol A, 17β-estradiol, Estron, 17α-ethynylestradiol and Nonylphenol (Table II), including any derivatives thereof. Commonly, estrogenic steroids will be present in wastewater comprising sewage.

According to an embodiment of the invention, such derivate(s) may also comprise one or more estrogenic substances provided by reaction of a (pre-) estrogenic substance directly or indirectly with an oxidizing agent, such as Cl_2. Said pre-estrogenic substance may comprise a substance or compound which is not estrogenic prior to said oxidation step, or a substance or compound which becomes more or less estrogenic upon said oxidation step.

According to one aspect of the present invention, a method is provided suitable for removing estrogenic substances in a (waste) water treatment plant. According to another aspect of the present invention, a method is provided suitable for removing estrogenic substances in a sewage treatment plant. According to another aspect of the present invention, a method is provided suitable for removing estrogenic substances in any system where estrogenic substances are undesired.

According to an embodiment, inactivation of said estrogenic substance(s) occurs after the steps of physical separation (primary treatment) and/or biological degradation (secondary treatment), and before the step of discharge of the treated water.

According to an embodiment, addition of a ClO_2 dose occurs before, after, or in combination with a tertiary treatment. The ClO2-treatment according to the invention can also be considered a tertiary treatment.

According to the invention, an amount or "dose" of ClO_2 can be added to the treated water to be discharged, said dose comprising less ClO_2 than the ClO_2-demand, and said dose being sufficient to reduce an estrogenic effect caused by one or more estrogenic substances, e.g. to below a threshold level. Such a dose can e.g. be around or less than 0.1%, 0.5%, 1%, 2%, 5%, 7.5%, 10%, 12%, 15%, 17%, 20%, 22%, 25%, 27%, 30%, 32%, 35%, 37%, 50%, 52%, 55%, 57%, 60%, 62%, 65%, 67%, 70%, 72%, 75%, 77%, 80%, 82%, 85%, 87%, 90%, 92%, 95%, 96%, 97%, 98%, 99%, 99.1%, 99.2%, 99.3%, 99.4%, 99.5%, 99.6%, 99.7%, 99.8%, 99.9%, 99.95%, 99.99%, 99.995%, or 99.999% of the ClO_2-demand. In another embodiment, the dose can be in the area or range of e.g. 0.1-1%; 1-5%, 5-10%, 10-20%; 20-30%, 30-40%, 40-50%, 50-60%, 70-80%, 80-90%, or 90-99.999% of the ClO_2-demand.

According to an embodiment, the ClO_2 concentration is reduced to less than 0.1 g per m^3 waste water in less than 30 or 60 seconds. Thus, the consumption of ClO_2 is a rapid process. The time from adding a dose of ClO_2 to the time point of reaching a ClO_2 concentration of 0.1 g/m^3, or less than 0.1 g/m^3 can also be called reaction time. In another embodiment, the ClO_2 concentration is reduced to 1.0 g, 0.5 g, 0.2, 0.1 g per m^3 waste water or less, in a reaction time of e.g. 30, 60, or 90 seconds or less, or 1, or 2 min, or less.

Providing a controlled dose of ClO_2, which is less/lower than the oxidant/ClO_2-demand which is capable of inactivating/removing/inactivating one or more undesired estrogenic substances e.g. within e.g. 30 or 60 seconds, or 1 or 2 min (also called "reaction time") is believed to advantageous compared to the addition of an excess of ClO_2, such as when ClO_2 is added with the purpose to disinfect water:

(1) According to the invention, the added ClO_2 will be completely or nearly completely removed from the wastewater/sewage before its release/discharge into the (water) environment. Common oxidants, including ClO_2 may have a toxic/negative effect on the environment, which could require a further treatment and/or means to remove/reduce the residual oxidant/ClO_2.

(2) Providing a smaller dose of ClO_2 per volume of treated water can be economically important, since the volumes of wastewater/sewage that have to be treated can be are very large. Thus the invention provided also a reduction and/or removal of estrogenic substances, whereby less ClO_2/oxidant is used than conventional methods and/or treatment facilities known in the art.

(3) It is also believed that, e.g. as a side effect, a treatment according to the invention may provide a measurable and a significant disinfection/decontamination of microorganisms present in the treated sewagewater to be discharged prior to ClO_2-addition. This effect, however, is

e.g. concentration and/or contamination dependent may not be as pronounced as when e.g. an oxidant/ClO_2-dose is added, said dose being higher/great/larger than the oxidant/ ClO_2-demand.

The reaction time is not limited and can depend on several factors and elements that are part of the present invention. In an embodiment of the invention, the reaction time is below or less than 60, 55, 50, 45, 40, 35, 30, 25, 20, 15, 10, 5, 2, or 1 seconds. In another embodiment, the reaction time is around 1, 2, 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, or 60 seconds. In a further embodiment, the reaction time is between 1 and 15, 15 and 30, 30 and 45, 45 and 60 seconds. In yet another embodiment, there reaction time is less than 10, 9, 8, 7, 6, 5, 4, 3, 2, or 1 minutes. In yet another embodiment, the reaction time is around 1, 1.5, 2, 2.5, 3, 3.5, 4, 4.5, 5, 6, 7, 8, 9, or 10 minutes. In still another embodiment, said reaction time is between 1 and 2, 2 and 3, 3 and 4, 4 and 5, 5 and 6, 6 and 7, 7 and 8, 8 and 9, or 9 and 10 minutes, or longer, if required or suitable.

According to an embodiment, the threshold level is as determined by a legal standard, or at which an estrogen-related biological effect is below the detection level of a biological assay. A suitable biological assay possesses a specific and measurable response to 17β-estradiol which can be mimicked by other chemicals by direct action via the steroid estrogen receptor. According to an embodiment of the invention, the threshold level is determined by a legal standard. The threshold level is related to an estrogen-related biological effect, such as near, about or below the detection level of a biological assay. In case of a change of legal standard, a person skilled in the art will be able to adapt the present method accordingly, such as e.g. increasing or decreasing reaction time and/or ClO_2 dose.

According to an embodiment, the threshold level corresponds to an estrogenic response concentration equivalent of 1.0; 0.1; or 0.05 ng/l 17β-

estradiol. The threshold level can also correspond to an estrogenic response concentration equivalent of exactly or around 0.01, 0.02, 0.03., 0.04, 0.05, 0.06, 0.07, 0.08, 0.09, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, 5.0, 6.0, 7.0, 8.0, 9.0, or 10 ng/l 17β-estradiol.

According to an embodiment of the invention the threshold level corresponds to an estrogenic response concentration equivalent to another estrogen than 17β-estradiol. In another embodiment, the estrogen is estradiol, estriol, or estrone. In a further embodiment, the estrogen is identical, or homologous to estradiol, estriol, or estrone from a vertebrate, mammal or human.

According to an embodiment, the ClO_2 dose is in the range of 0.1-20, or 0.1-8 g ClO_2 per m^3; or per liter wastewater. The ClO_2 dose is in the range of 0.1-100, 0.5-50, 0.75-30, 1-20, 1-15, 1-10, 1-8, 1-7. 1-6, 1-5, 1-4, 2-4 g ClO_2 per m^3 wastewater/sewage or water to be treated. According to another embodiment, the ClO_2 dose is exactly, or around 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, 1.25, 1.50, 1.75, 2.0, 2.25, 2.50, 2.75, 3.0, 3.25, 3.50, 3.75, 4.0, 4.25, 4.50, 4.75, 5.0, 5.25, 5.50, 5.75, 6.0, 6.25, 6.50, 6.75, 7.0, 7.25, 7.50, 7.75, 8.0, 8.25, 8.50, 8.75, 9.0, 9.25, 9.50, 9.75, 10.0, 10.5, 11.0, 11.5, 12.0, 12.5, 13.0, 13.5, 14.0, 14.5, 15.0, 16, 17, 18, 19, 20, 22, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, 95, 100 g ClO_2 per m^3 wastewater/sewage or water to be treated.

According to an embodiment of the invention, the ClO_2 concentration is reduced to less than 0.01, 0.02, 0.03., 0.04, 0.05, 0.06, 0.07, 0.08, 0.09, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, 5.0, 6.0, 7.0, 8.0, 9.0, or 10 g ClO_2 per m^3 wastewater/sewage in less than 10, 9, 8, 7, 6, 5, 4, 3, 2, or 1 minutes, or less than 60, 55, 50, 45, 40, 35, 30, 25, 20, 15, 10, 5, 2, or 1 seconds.

According to an embodiment, said estrogenic substance(s) is/are removed at a specific removal rate, said removal rate being at least 90%, 95%, 99%, 99.5%, 99.9% or more. One or more estrogenic substances can also be removed at a minimal specific removal rate ($r_{\%}$), said removal rate being at least or more than 50%, 55%, 60%, 65%, 70%, 75%, 80%, 85%, 87%, 90%, 92%, 93%, 94%, 95%, 96%, 97%, 98%, 99%, 99.1%, 99.2%, 99.3%, 99.4%, 99.5%, 99.6%, 99.7%, 99.8%, 99.9%, 99.95%, 99.99%, 99.995%, or 99.999%.

According to an embodiment, the wastewater is domestic, agricultural, hospital, or industrial waste water, or any mixture and/or combination thereof. The waste water can also be derived from domestic, agricultural, or industrial waste water, or any combination thereof. This wastewater can e.g. comprise one or more estrogenic substances selected from the group consisting of one or more of estrogenic stereoid(s), 17β estradiol, Estron, 17α ethynylestradiol, Bisphenol A, and Nonylphenol, including any estrogenic derivative(s) and combination(s) thereof. The wastewater may also comprises a significant amount of sewage, such as more than 5%, 10%, 20%, 30%, 40%, 50%, 60%, 70%, 80%, 90%, or more than 90% sewage. Thus, according to the invention, said (waste)water/sewage treatment may comprise treatment of sewage and/or any waste watercomprising sewage. The water to be treated according to the invention may comprise or be derived from raw influent or sewage comprising e.g. household waste, liquid from toilets, baths, showers, kitchens, sinks, and so forth. It may also comprise what is commonly disposed via sewers. The water to be treated may also comprise fluids from industry and commerce, as well as household waste, including greywater and blackwater. The sewage/waste water may also comprise surface water, e.g. from roofs or hard-standing areas, as well as stormwater, e.g. as a result of water from rainfall running over the surface of roofs and the ground, whereby the water may pick up various contaminants, e.g. soil particles and other sediment, heavy metals, organic compounds, animal waste, and oil and

grease. According to a further embodiment, the wastewater is not solely greywater, such as wastewater comprising sewage or any other agricultural or industrial waste water.

According to an embodiment, the (waste)water or sewage has not been subjected to addition or treatment with an oxidant, such as ozone or ClO_2, e.g. as a disinfecting step prior to a ClO_2-mediated removal of estrogenic substances according to the invention before said step of discharge of the treated water from the wastewater/sewage plant. According to another embodiment, said (waste)water or a part or portion of said wastewater and/or sewage has been subjected to an UV-treatment, such as a UV-mediated disinfecting step, prior to a ClO_2-mediated removal of estrogenic substances according to the invention before said step of discharge of the treated water from the wastewater/sewage treatment plant.

According to an embodiment, the water treated with ClO_2 according to the invention can be selected from the group comprising or consisting of fully treated wastewater, effluent, waste water, or water to be discharged. According to another embodiment, the wastewater or water to be discharged is fully treated wastewater.

The pH of said water treated with ClO_2 according to the invention has a pH of $\leq$ 8.5, $\leq$ 8.0, $\leq$ 7.5, $\leq$ 7.0, or $\leq$ 6.5. In another embodiment, the pH is in the range of pH 6.0 to 9.0, 6.0 to 8.5, 6.0 to 7.5, 6.5 to 7.5, or 7.0 to 7.5. In a further embodiment, the pH is around pH 6.0, 6.5, 7.0, 7.5, 8.0, or 8.5. According to a further embodiment, the pH of the wastewater or water to be discharged is below pH 8.5, pH 8.0, pH 7.5, pH 7.0, or pH 6.5 before or at the point of ClO_2-dosage according to the invention.

According to an embodiment, feedback means are provided adapted to measure/assess the estrogenic effect, and providing the appropriate ClO_2

dose based on the output of said measurement/assessment of the estrogenic effect and the current ClO_2-demand. Such feedback means can also be adapted for indirectly measuring/assessing the content of reactive organic matter based on the absorption of UV light, e.g. in the spectral range 200-400, 210-380, or 240-270nm, or based one or more fluorescence wavelength(s) emitted upon exciting waste water with light in the UV or VIS range, such as a wavelength in the range of 200-800 nm, 200-400, 210-380, or 240-270nm, and providing the appropriate ClO_2-dose based on the output of said measurement/assessment and the current ClO_2-demand. Thus, according to an embodiment of the invention, a method comprising a feedback means is provided for measuring/assessing the estrogenic effect, and providing the appropriate ClO_2 dose based on the output of said measurement/assessment of the estrogenic effect and the current ClO_2-demand. According to another embodiment, said feedback means is adapted to indirectly measure/assess the content of reactive organic matter based on the absorption of UV light in the spectral range 270-240 nm, or one or more fluorescence wavelength(s) emitted upon exciting wastewater/sewage with light in the range 270-240 nm, and providing the appropriate ClO_2 dose based on the output of said measurement/assessment and the current ClO_2-demand.

According to an embodiment, the method comprises ClO_2 providing means comprising flow controlling means adapted to provide a controlled flow of ClO_2 in water or a gas phase containing ClO_2, dosing means adapted to provide ClO_2 in a controlled dose/concentration, and feed-back means. Such ClO_2 providing means may comprise one or more of flow controlling means adapted to provide a controlled flow of ClO_2 in water or a gas phase containing ClO_2, dosing means adapted to provide ClO_2 in a controlled dose/concentration, feed-back means, and any combination thereof.

According to an embodiment, said ClO_2 providing means provide ClO_2 as a function of, or are proportional to one or more of:

(a) flow of waste water;

(b) level of estrogenic substance(s);

(c) ClO_2-demand; and/or

(d) feedback means.

According to an embodiment of the invention, said ClO_2 providing means provide ClO_2 as a function of or proportional to one or more of: (a) flow of waste water; (b) level of one or more estrogenic substance(s); (c) oxidant/ ClO_2-demand; (d) feedback means.

Another aspect of the invention concerns the use of ClO_2 providing means and/or feed-back means according to any one or more of the previous embodiments in a water/sewage treatment plant.

A further aspect of the invention relates to a water treatment plant adapted to removing estrogenic substances according to any one or more of the previous aspects and/or embodiments.

The following section concerns embodiments comprising ClO_2-addition (i) after, (ii) before an aeration stair, as well as (iii) optimization of a ClO_2-dose to the ClO_2-demand (oxidant demand) of a wastewater, sewage and/or wastewater comprising sewage:

(i) ClO_2-addition after aeration stair

A sewage treatment plant consisting of primary to tertiary treatment steps for both advanced nitrogen and phosphorous removal is provided with a ClO_2 based treatment for estrogenic chemicals according to the invention. This may comprise that the point of ClO_2-addition/treatment is e.g. chosen to be positioned after an aeration stair, since a treatment plant with such a device

often comprises a long effluent pipe with a water retention time higher than e.g. 10 min before the water is discharged into the environment.

To optimize a treatment according to the invention, water samples can be collected from the outlet of the aeration stairs at regular interval over a longer time period, such as e.g. every day for 120 days, and the reactivity of ClO_2 can be determined experimentally as described e.g. in the definition of oxidant/ClO_2-demand. It can be advantageous that in the period of collecting water samples, the sewage treatment plant experiences e. g. two or more rain events which are typical for the highest precipitation events normally found during a year in the sewer system, which may increase the flow significantly. The point of including rain events in the period of determining the oxidant/ClO_2-demand and variation in the oxidant/ClO_2-demand can e.g. be that dilution of the sewage with rainwater may result in water with a lower oxidant/ClO_2-demand.

For example, it may be found that the oxidant/ClO_2-demand in 30 seconds varies e.g. between 5 and 8 mg/l, the oxidant/ClO_2-demand in 10 min is e.g. between 7 and 9 mg/L, the oxidant/ClO_2-demand in 120 min and 8 hours is comparable, and e.g. between 8 and 12 mg/l. Further, the flow of water from the plant could e.g. be between 90 and 110 m3 per hour in dry conditions, and during the strongest rain events which may occur e.g. in the plants 10 years history of existence, the peak flow could be 230 m3 per hour.

According to this example, a treatment facility according to the invention may be provided with a ClO_2 generator capable of providing e.g. a 4.5 g/l stock solution of ClO_2 into a storage tank. Further, a variable flow dosing pump could be used, capable of transferring or pumping defined volumes of the ClO_2 stock solution over a defined period of time into the chosen dosing point in the wastewater/sewage stream.

The delivery point, where the ClO_2 solution is mixed into the wastewater/sewage may be chosen to be e.g. 100 cm or more into the effluent pipe after the aeration steps to e.g. avoid mixing of ClO_2 into the aeration stairs. At the delivery point, such a pipe may have a diameter of 40 cm. The ClO_2-stock solution could e.g. be divided, such as equally into one or more nozzles, such as two, three, four, five, six or more which could e.g. be spaced with one nozzle in the centre of the pipe and the others e.g. spaced equally between the centre and the wall of the pipe in order to provide an even distribution of ClO_2 into the wastewater/sewage. The number and distribution of nozzles used for the provision and distribution of ClO_2 into the treated water can be optimized in each type of wastewater/ sewage according to how quickly the ClO_2 reacts with the water, the diameter of the pipe and the turbulence of the treated water at the dosing point, so that all the water comes in contact with ClO_2 before the ClO_2 is consumed. Such optimization can be performed using methods and means known in the art.

The dosing pump can e.g. be controlled by a signal from a flow meter measuring the total flow of sewage from the plant, so that when for example the flow is 100 m^3/h, the dosing pump delivers e.g. 100 ml per hour of the stock solution, providing thereby e.g. a ClO_2-dose of 4.5 g/m^3. If the flow of water decreases to 90 m3 per hour, the dosing pump would delivers 90 ml per hour of stock solution, whereby the ClO_2 dose remains constant at 4.5 g/m^3. The dosing pump can be dimensioned so that the maximal pumping rate is sufficient to maintain a constant dosing during the high flow which occurs during rain events, which in the above example would be 230 ml per hour.

(ii) ClO_2-addition before aeration stair

A sewage treatment plant comprising primary, secondary and/or tertiary treatment steps for e.g. both advanced nitrogen and phosphorous removal

could be expanded with a ClO_2-based treatment for estrogenic chemicals according to the invention as follows:

The point of ClO_2-provision could also be chosen to be near or at the point of inflow into the aeration stair(s), e.g. when the effluent in the effluent pipe from the plant has a short retention time of e.g. less than 1 min before the water is released into the environment, while the aeration stairs have a longer retention time of e.g. 6 min with normal flow, and not less than e.g. 3 min during a large or heavy rain event. Water samples could be collected from the inlet to the aeration stairs at regular interval over a longer time period, such as e.g. every 3rd day for 360 days, and the reactivity of ClO_2 could be determined experimentally as described in the section Materials and methods, definition of oxidant/ClO_2-demand, or elsewhere. In the period of collecting water samples the sewage treatment plant should experience e.g. several, such as two, three or more rain events, which are typical for the largest rain events, which are expected to occur during a year on that location.

As an example, the oxidant/ClO_2-demand in 30 seconds could vary e.g. between 2 and 8 mg/l, the oxidant/ClO_2-demand in 10 min e.g. between 3 and 9 mg/l, the oxidant/ClO_2-demand in 120 min and 8 hours could e.g. be between 5 and 11 mg/l. The flow of water from the plant could be for example between 850 and 1200 m3 per hour in dry conditions, and during the strongest rain which occurred in the plants 10 years history of existence, the peak flow could be 1900 m^3/h.

According to this a treatment facility may be provided with a ClO_2 generator capable of producing e.g. a 9 g/l solution of ClO_2 with a variable output flow of maximally 1000 ml/h, which is directly connected to the dosing point in the wastewater/sewage stream. The point there the ClO_2 solution is mixed into the wastewater/sewage could be chosen to be located upstream, e.g. 50 cm upstream or more in the pipe leading into the aeration stairs, whereby a

sufficient and/or equal mixing could be provided. The output from the ClO_2 generator could be controlled by a signal from a flow meter measuring the total flow of sewage from the plant, in order to provide a constant or near-constant dose of ClO_2, such as e.g. 4.5 g/m^3 using principles as shown e.g. in Example (i).

(iii) Optimization of ClO_2-dose to the oxidant/ClO_2-emand of a wastewater/sewage

In order to continuously optimize the dose to the variability of the ClO_2-demand a wastewater/sewagewater, ClO_2–providing means according to the invention, such as described in example A or B could be expanded provide a flow and/or oxidant/ClO_2-dependent dosage of ClO_2. Thereto, as an example, a device can be provided adapted to be capable of determining the e.g. 30 second oxidant/ClO_2-demand. According to an embodiment of the invention, this could e.g. be achieved by adding e.g. 10 mg/l ClO_2 to a small flow of water taken by a pump just before the dosing point of the treatment, said small flow of water being lead through a thin tube of a length which is matched to the flow rate of the pump to give e.g. a residence time of e.g. 30 seconds, before a device adapted to be capable of measuring, monitoring or assessing the ClO_2-concentration is determining the residual concentration of ClO_2. The oxidant/ClO_2-demand can thus be measured online as the difference between the initial added concentration e.g. 10 mg/l ClO_2 and the residual concentration after the reaction time and the target dose of the treatment can then be reset to a fraction of the measured oxidant/ClO_2-demand which can be 70 % or any other ClO_2-dose which are found by experience with the specific plant over time.

The present invention relates also to one or more means and method(s) for a ClO_2-treatment of a wastewater/sewage, comprising means for and/or the step of continuously adjusting a ClO_2-dose according to an actual oxidant/ClO_2-demand.

According to an embodiment of the invention, dosing of ClO_2 can be regulated according to an actual ClO_2 consumption in a specific time. This continuous analysis can e.g. be achieved by providing a device comprising a pump which draws an defined flow (A) of the wastewater/sewage and a second pump which draws an defined flow (B) of ClO_2 stock solution from a dosing means, said stock solution having a concentration (C). Both flows A and B are mixed and channelled in e.g. a tube/pipe with a defined length which could e.g. be matched to the combined flow to give a specific/defined retention time in the tube/pipe. After the tube/pipe, the mixture enters a ClO_2-determing means, such as a ClO_2-sensor, adapted to and/or suitable for an appropriate measurement/assessment of the concentration of ClO_2 (D) in the expected concentration range.

The oxidant consumption/demand (E) as ClO_2 in the specified time can then be calculated as: E = B*C/(A+B)-D

The dosing device/means/arrangement which delivers ClO_2 to the wastewater/sewage can be provided with regulating means adapted to deliver a controlled/defined ClO_2 dose, such as a constant fraction F of E, whereby F is greater than zero, and e.g. smaller than one, i.e. $0 < F < 1$. In another embodiment, F could also be around 1 or greater than 1.

It is obvious that any variation or inaccurateness in the concentration (C) of the ClO_2 stock solution from the dosing equipment which may occur over time would be corrected as well, together with any variation in the oxidant consumption of the treated wastewater/sewage.

According to an embodiment of the invention, the analytical principle of a ClO_2-sensor or ClO_2-measuring means may comprise or be based on light absorbance at a specific wavelength, fluorescence or reaction by oxidation

with a chemical which possess a different colour in the oxidized state than in the reduced state of said chemical.

Several principles of measuring the ClO_2 residual concentration are believed suitable and/or applicable. According to an embodiment of the invention, ClO_2 concentration quantification means/device may be provided by providing into a water sample to be analyzed, e.g. via a dosage pump, a pH-buffer solution to give an optimal pH for the oxidation reaction of N,N-diethyl-p-phenylenediamine at a defined time point/reaction time. Such a reaction is known in the art, and N,N-diethyl-p-phenylenediamine is believed to be rapidly and quantitatively oxidized by the remaining ClO_2 in a sample. The oxidized derivative/form of N,N-diethyl-p-phenylenediamine is believed to absorb light strongly at ~510 nm and therefore e.g. a spectrophotometer adapted to measure light absorbance at ~515 nm (or in the range 490-555 nm) of the mixture will provide a signal which can be (linearly) correlated to the concentration of ClO_2 in the sample. Such devices suitable for automatic application are e.g. available from e.g. Alldos GmbH and other manufacturer.

According to one embodiment of the invention, an internal standard is used. Suitable internal standards may comprise e.g. iso-propyl 4-hydroxybenzoate (isoPP), CAS 4191-73-5; bisphenol A deuterated (BPA-d6), CAS 86588-58-1; n-nonylphenol (n-NP), CAS 104-40-5; E2-A 17β-estradiol 17-acetate, CAS 1743-60-8. Without wanting to be bound by any theory, it is believed that such internal standards are not common wastewater/sewage contaminants.

An embodiment of the invention concerns a method for removing estrogenic substances in a sewage treatment plant, wherein said removal of estrogenic substances occurs after the steps of primary and secondary treatment, and before the step of discharge of the treated water from the waste water plant, wherein said method comprises the step of adding a dose of ClO_2 to the treated water to be discharged, said dose comprising less ClO_2 than the

ClO_2-demand, i.e. the amount of ClO_2 which can be consumed by reaction with any material within a defined reaction time, e.g. 60 seconds, of said treated water to be discharged, and said dose being sufficient to reduce an estrogenic effect caused by said estrogenic substances to below a defined threshold level.

An embodiment of the invention pertains to the use of ClO_2 providing means and/or feed-back means for performing the method of removing estrogenic substances in a sewage treatment plant, wherein said removal of estrogenic substances occurs after the steps of primary and secondary treatment, and before the step of discharge of the treated water from the waste water plant, wherein a dose of ClO_2 is added to the treated water to be discharged, said dose comprising less ClO_2 than the ClO_2-demand, i.e. the amount of ClO_2 which can be consumed by reaction with any material within a defined reaction time, such 60 seconds, of said treated water to be discharged, and said dose being sufficient to reduce an estrogenic effect caused by said estrogenic substances to below a defined threshold level.

An embodiment of the invention relates to a sewage treatment plant adapted to removing estrogenic substances, wherein said removal of estrogenic substances occurs after the steps of primary and secondary treatment, and before the step of discharge of the treated water from the sewage water plant, wherein a dose of ClO_2 is added to the treated water to be discharged, said dose comprising less ClO_2 than the ClO_2-demand, i.e. the amount of ClO_2 which can be consumed by reaction with any material within a defined reaction time, such as 60 seconds, of said treated water to be discharged, and said dose being sufficient to reduce an estrogenic effect caused by said estrogenic substances to below a defined threshold level.

The present invention is disclosed in this specification, comprising definitions, embodiments, aspects, examples, claims, and figures. Furthermore, these

are to be considered as being combinable and/or selectable, including e.g. any meaningful permutation of any definition, embodiment, aspect, example, claim, and/or figures. Thus any such combination and/or selection is to be regarded as being disclosed within the current specification, even if not indicated explicitly.

The current invention is further described in the following Examples, which are not to be construed as limiting for the scope of the present invention.

EXAMPLES

Materials and methods

Chemicals

Estrogenic chemicals which are spiked to wastewater for treatment experiment were all from Sigma, Denmark and were purchased as analytical standards. Table I provides further information concerning chemicals, including abbreviations used herein.

A stock solution of ClO_2 was prepared by mixing adding to 400 ml demineralised water 25 ml 9 %-solution (w/w) of hydrochloric acid and 25 ml 7,6 % $NaClO_2$-solutions (w/w). The reaction was allowed to run for 12 h before diluting the stock to 1000 ml with demineralised. The concentration of the stock solution was measured before each experiment to determine the exact concentration.

Analytical methods

Concentration determination of ClO_2

Chlorine dioxide was quantified photometrically by oxidation of DPD (N,N-diethyl-p-phenylenediamine) which was quantified by an Allcon

spectrophotometer from Alldos GmbH (Germany) according to the standard curve provided by the manufacturer. The method had a functional measuring range from 0.03 to 10 mg/L.

Chemical Oxygen Demand (COD)

Analysis of chemical oxygen demand (COD) was performed essentially as described in the Danish Standard DS 217:1991 "Water examination. Determination of chemical oxygen demand in water COD_{Cr} with dichromate."

Concentration determination of estrogenic chemicals

Subsamples of treated water of 250 ml were filtered and extracted on 500 mg C18 solid phase extraction cartridges from Varian Inc. The extracts were eluted from the cartridge with 5 ml acetone. The volume was reduced to 200 µl by nitrogen evaporation before extracts were cleaned on a silica column using heptane/acetone (65:35 v/v) as eluent. Each extract was split and one of the extracts of each sample was derivatised by MSTFA. Both extracts were quantified with a Varian GC 3800 with Saturn 2200 iontrap (MS-MS) using a FactorFour Capillary column VF-5ms 30mx0.25 mm. PTV-injector 1079. A temperature program was used from 105 to 300 ºC and retention times were from 8 to 21 min. All measured chemicals were identified based on at least two characteristic daughter ions which were collected from fractionating a characteristic mother ion. The details of the quantification method for the non-derivatised and derivatised extracts were essentially as described in the papers by Andersen et al., 2001 and 2007.

Estrogen equivalent potency

500 ml samples of wastewater were extracted into 500 mg C18 solid phase extraction cartridges from Varian Inc. The extracts were eluted in acetone and serially diluted in a growth media for yeast cells. The dilutions are incubated with an estrogen responsive yeast cell for 72 h. The estrogenic effect is quantified by measuring the development of a red dye which is produced by the yeast cells with an enzyme which is produced proportionally

to the estrogenic concentration in the cells (YES assay). For quantification of the estrogenic effect a standard curve is made from a stock solution of 17beta-estradiol (E2). The details of the method are essentially as seen in Körner et al. (2001).

Experiments

Effluent samples were taken from two sewage treatment plants which are known to have either a high COD (Lynetten sewage treatment plant) typically around 40 mg/L, or a low COD (Lundtofte sewage treatment plant) typically around 13 mg/L. On the day of collecting the samples, the pH of both effluents was measured to be 7.2 ±0.1.

In order to determine the reactivity of the above effluents, experiments were conducted where 8 mg/L ClO_2 were added, and the ClO_2 concentration profile was followed over two hours.

In another experiment, both effluent samples were spiked with the investigated estrogenic chemicals to a concentration of 1.0 µg/L each, except for the three steroid estrogens E1, E2 and EE2 which were only spiked to a concentration of 0.4 µg/L each. The two effluents were divided into sub-samples, which were each treated with 0, 0.5, 2.5, 3.75, 5.0 or 10 mg/L of ClO_2.

Samples were allowed to react for 8 h at room temperature. After the reaction pH was measured before the samples were preserved by adding a phosphate buffer to give pH = 2.9 ±0.1 and an excess of sodium sulphite relative to ClO_2 added.

Each treatment of the two water types was analysed for concentrations of the spiked chemicals and estrogenic effect by the YES assay.

Results and discussion

Reaction of effluents with ClO_2

Concentration profiles of ClO_2 consumption by the two effluents is shown in Figure 2. It is observed that for both effluents there is initially a rapid consumption of ClO_2 around 4.5 mg/L within the first 30 seconds followed by a slower removal in the next 120 min.

The effluent from Lynetten sewage treatment plant had a COD of ~40 mg/L, while the effluent from Lundtofte sewage treatment plant had a COD of ~15 mg/L. If it is assumed that oxidation by ClO_2 follows reaction (1), the COD of 40 mg/L equals a ClO_2 consumption of 150 mg/L for total oxidation of Lynetten sewage treatment plant; similarly, the consumption of Lundtofte sewage treatment plant effluent would be 65 mg/L ClO_2.

It is thus seen that the very fast initial consumption reaction with ClO_2 in the first reaction in the first 0.5 min after addition represents a very small fraction of the total ClO_2-demand of the water around 1.2 % and 3.5 %, respectively, for Lynetten and Lundtofte sewage treatment plant effluents.

Degradation of target chemicals from effluents by ClO_2

The remaining concentrations of spiked steroid estrogens in Lundtofte and Lynetten effluents after treatment with different doses of ClO_2 are shown in Figure 3. In Lundtofte effluent, 50% of the steroid estrogens were removed already by 0.5 mg/L ClO_2, while 1.25 mg/L ClO_2 were required to get a significant removal in Lynette sewage treatment plant effluent, and removal to or below detection limit required a total of 2.5 mg/L, and 3.75 mg/L, respectively.

Removal of industrial phenols and parabens (see Figure 4) required slightly higher ClO_2 doses for removal for both effluents. Thus 3.75 mg/L was

needed to remove all in both effluent types, but the trend that that effluent from Lynetten sewage treatment plant, with higher natural COD, required more treatment was evident then comparing the removal at the 2.5 mg/L treatment level.

For sunscreens (see Figure 5) BP-3 and BP-7 behaved similar to the industrial phenols and parabens, which is not surprising, since they contain a similar phenolic group, while HMS and OD-PABA appears more resistant to treatment.

Upon analysis by the Yeast Estrogen Screen (YES) assay (see Figure 6), the results seen above and the trends for single chemicals were confirmed. For the spiked Lundtofte effluent, a significant removal of estrogenic potency was evident by treatment with 0.50 mg/L ClO_2, while ~95% removal was seen upon treatment with 1.25 mg/L ClO_2-treatment. Treatment with 2.50 mg/L ClO_2 and higher showed removal to the level of the blank sample (>99% at 95% confidence level).

For Lynetten effluent, no significant removal was evident by treatment with 0.5 and 1.25 mg/L ClO_2, while ~95% removal was achieved by treatment with 2.5 mg/L ClO_2. Treatment with 3.75 mg/L ClO_2 and higher result in removal to the level of the blank sample (>99% at 95% confidence level).

It appears that removal of estrogenic potency follows the chemical removal of steroid estrogens more than the other compounds, which agrees with the much higher potency of steroid estrogens compared to the other investigated estrogenic chemicals.

Perspectives for treatment of effluents

From the concentration profile experiments it was found that both effluents consumed 4.3 mg ClO_2 per litre treated sewage in the first 30 seconds after treatment, while addition of 3.75 mg ClO_2 per litre treated sewage could remove 400 ng/L of steroid estrogens and 1.0 µg/L of the estrogenic phenols and parabens and the relevant sunscreens BP-3 and BP-7.

It is therefore suggested that an end-of-pipe treatment for estrogens in municipal sewage could be constructed by injecting e.g. 2-4 mg/L of ClO_2 into the flow of treated sewage from the waste water treatment plant at a place there at least e.g. 30 seconds reaction time is allowed before the effluents is reach the recipient water. This could be immediately after the aeration stairs of many conventional waste water treatment plants. Such a ClO_2-treatment could e.g. be performed after the step(s) of primary and/or secondary treatment, and before the step of discharge of the treated water from the waste water plant

It is anticipated that the reactivity of sewage may vary over time, for example during or after heavy rain-falls or flooding. It is conceivable that the reactivity towards ClO_2 in terms of reaction rate and consumed concentration is constant or almost constant per measure of time or volume of effluent. Furthermore, also seasonal variations could also be expected, such as higher concentrations of sun-screen during summer than during winter, etc.

According to one embodiment of the invention, dosage of ClO_2 is proportionally to the reading of the flow meter on the effluent of the waste water treatment plant (for example, most facilities in Denmark have a digital readout of flow in the effluent for regulatory purposes). According to another embodiment, ClO_2-dosage is constant or almost constant per volume of effluent. In a further embodiment, ClO_2-dosage is independent of precipitation according to the ClO_2 reactivity during dry periods.

Without being bound by any theory, with respect to the fate of chlorite in treated sewage, and possibly surface waters, it is believed that chlorite is reduced in sewage and surface water over time, such as according to reaction (2). It is believed that this process is not as fast as the reduction of ClO_2, therefore it should be considered if the chlorite concentration resulting from the treatment is tolerable for the environment.

Determination of ClO_2-demand

In order to determine the ClO_2-demand of a water sample, an excess of ClO_2, e.g. in the order of magnitude of 1.5, or 3 times the amount of ClO_2 expected to be consumed within e.g. 1, 2, 4, or 6 h, is added to said water. The 1, 2, 4, or 6h ClO_2-demand is determined by measuring the remaining oxidant after 1, 2, 4 or 6 hours and subtract this from the amount added. To illustrate this further, if 10 mg ClO_2 were added to a water sample of 1 L, and after 10 min the concentration of ClO_2 was measured to be 4 mg/L, 2 mg/L after 60 min, and 1.5 mg/L after 120 min and 240 min, than the ClO_2-demand (10 min) would be 6 mg/L ClO_2, ClO_2-demand 60 min = 8 mg/L, 120 min and 240 min = 8.5 mg/L. The total ClO_2-demand would also be 8.5 mg/l.

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Table I. List of chemical compositions according to the invention.

Group	Abbreviation	Chemical name[(1)]	CAS[(1)]
Parabens	**MP**	Methyl 4-hydroxybenzoate	99-76-3
	EP	Ethyl 4-hydroxybenzoate	120-47-8
	PP	Propyl 4-hydroxybenzoate	94-13-3
	isoBP	isoButyl 4-hydroxybenzoate	4247-02-3
	BP	Butyl 4-hydroxybenzoate	94-26-8
		Pentylparben	*6521-29-5*
		Hexylparaben	*1083-27-8*
		Heptylparaben	*1085-12-7*
		Octylparaben	*1219-38-1*
Industrial phenols	**BPA**	Bisphenol A	80-05-7
	isoNP	4-Nonylphenol	84852-15-3
	OP	4-tert-Octylphenol	140-66-9
Sun screen	**OMC**	2-Ethylhexyl trans-4-methoxycinnamat	83834-59-7
	BP-3	2-Hydroxy-4-methoxybenzophenon	131-57-7
	BP-7	5-Chloro-2-hydroxybenzophenone	85-19-8
	HMS	Homosalate	118-56-9
	OD-PABA	2-Ethylhexyl 4-(dimethylamino)benzoate	21245-02-3
	4-MBC	3-(4'-methylbenzylidene) camphor	36861-47-9

Table I (continued)

Group	Abbreviation	Chemical name	CAS
Steroid estrogens	**E1**	Estrone	53-16-7
	E2	17β-Estradiol	50-28-2
	EE2	17α-Ethynyl estradiol	57-63-6
		17α-Estradiol	*57-91-0*
		Estriol	*50-27-1*
		Mestranol	*72-33-3*
		2-hydroxyestrone	*362-06-1*
		2-hydroxy-17β-Estradiol	*362-05-0*
		17β-Estradiol 17-(β-D-gluconide)	*15087-02-2*
		Estriol 17-(β-D-glucoronide)	*7219-89-8*
		Estriol 16α-(β-D-glucuronide)	*1852-50-2*
Phthalates		*Benzyl-n-butylphthalate*	*85-68-7*
		Di-n-butylphthalate	*84-74-2*
		di-sec-octyl phthalate	*117-81-7*
Natural compounds[2]		*Genistein*	*446-72-0*
		β-sitosterol	*83-46-5*
		Zearalenon	*17924-92-4*
		Zearalenol	*36455-72-8*

Table I (continued)

Group	Abbreviation	Chemical name	CAS
Pesticides		*Sumithrin*	*26002-80-2*
		Fenvalerate	*51630-58-1*
		d-Trans Allethrin	*584-79-2*
		Permethrin	*52645-53-1*
		Fenarimol	*60168-88-9*
		Triadimefon	*43121-43-3*
		Triadimenol	*55219-65-3*
		1-hydroxychlordene	*2597-11-7]*
		p,p-DDT	*50-29-3*
		Endosulfan	*115-29-7*

(1) Compositions listed in italics are believed not to be included in example 1, but are believed to be according to contributing to estrogenicity in wastewater/ sewage. One or more of these compounds may also be inactivated by ClO_2-treatment according to the present invention.

(2) Natural compounds could e.g. be found in or derived from plants and/or fungi.

Table II Estrogenic compounds with a pKa > 10

EDCs	pK_a	log K_{ow}	log K_{oc}
Bisphenol A	10.2–10.3[1]	3.4[2]	2.50–3.18[2]
17β-estradiol	10.4[1]	3.94[4]–4.03[3]	3.5[4]
Estron	10.4[1]	3.43[4]	3.5[4]
Estriol	n.d.	2.81[4]	3.5[4]
17α-ethinylestradiol	10.46–10.70[1]	2.83[3]; 4.15[4]	3.8[4]
Nonylphenol	10–12[1]	3.28–4.48[5]	4.0[6]; 5.6[7]

From Nghiem L. D and Schäfer A. I. (2006)

CLAIMS

1. A method of inactivating one or more estrogenic substance(s) in a wastewater treatment plant, said method comprising a step of adding a dose of ClO_2 to the water to be discharged, and said ClO_2-dose being less than the ClO_2-demand of the water to be discharged.

2. A method of treating wastewater, said method comprising the steps of:
- determining the ClO_2–demand of a water sample to be discharged;
- adding a dose of ClO_2 to the water to be discharged, said dose being less than ClO_2–demand of the water to be discharged; and
- inactivating one or more estrogenic substance(s) in the water to be discharged.

3. A method according to claim 1 or 2, wherein the wastewater is not solely greywater.

4. A method according to any one of the preceding claims, wherein the pK_a value of said estrogenic substance(s) is greater than 9.0, 9.5, or 10.0.

5. A method according to any one of the preceding claims, wherein said inactivation of said estrogenic substance(s) occurs after the steps of physical separation (primary treatment) and/or biological degradation (secondary treatment), and before the step of discharge of the treated water.

6. A method according to any one of the preceding claims, wherein said addition of a ClO_2 dose occurs before, after, or in combination with a tertiary treatment.

7. A method according to any one of the preceding claims, wherein said inactivation of said estrogenic substance(s) occurs within less than 2 minutes, or less than 1 minute after addition of the ClO_2-dose.

8. A method according to any one of the preceding claims, wherein the ClO_2-demand is the amount of ClO_2 which is consumed when added to a defined volume of said treated water to be discharged within a defined reaction time, such as 1 litre and 1 hour.

9. A method according to any one of the preceding claims, wherein said dose is sufficient to completely eliminate an estrogenic effect of the discharged water (effluent), or to remove the estrogenic effect of the effluent to below a defined threshold level.

10. A method according to claim 9, wherein the threshold level is as determined by a legal standard, or at which an estrogen-related biological effect is below the detection level of a biological assay, and optionally wherein said biological assay has a specific and measurable response to 17β-estradiol which can be mimicked by other chemicals by direct action via the steroid estrogen receptor.

11. A method according to any one of the preceding claims, wherein the estrogenic substance(s) is/are selected from the group consisting of one or more of estrogenic stereoid(s), 17β estradiol, Estron, 17α ethynylestradiol, Bisphenol A, and Nonylphenol, including any estrogenic derivative(s) and combination(s) thereof.

12. A. method according to any one of the preceding claims, wherein the threshold level corresponds to an estrogenic response concentration equivalent of 1.0; 0.1; or 0.05 ng/l 17β-estradiol.

13. A method according to any one of the preceding claims, wherein said ClO_2 dose is in the range of 0.1-20, or 0.1-8 g ClO_2 per m^3 wastewater.

14. A method according to any one of the preceding claims, wherein the ClO_2 concentration is reduced to less than 0.1 g per m^3 waste water in less than 30 or 60 seconds.

15. A method according to any one of the preceding claims, wherein estrogenic substance(s) is/are removed at a specific removal rate, said removal rate being at least 90%, 95%, 99%, 99.5%, 99.9% or more.

16. A method according to any one of the preceding claims, wherein said wastewater comprises a significant amount of sewage.

17. A method according to any one of the preceding claims, wherein said wastewater is domestic, agricultural, hospital, or industrial waste water, or any combination thereof.

18. A method according to any one of the preceding claims, wherein the wastewater or water to be discharged is fully treated wastewater.

19. A method according to any one of the preceding claims, wherein the pH of said wastewater or water to be discharged is below pH 8.5, pH 8.0, pH 7.5, pH 7.0, or pH 6.5 before or at the point of ClO_2-dosage.

20. A method according to any one of the preceding claims, wherein the ClO_2-dose is 70%, 50%, or less than 50% of said ClO_2-demand.

21. A method according to any one of the preceding claims, said method comprising a feedback means adapted for measuring/assessing the estrogenic effect, and providing the appropriate ClO_2 dose based on the output of said measurement/assessment of the estrogenic effect and the current ClO_2-demand.

22. A method according to any one of the preceding claims, said method comprising a feedback means adapted for indirectly measuring/assessing the content of reactive organic matter based on the absorption of UV light in the spectral range 380-210 nm, or one or more fluorescence wavelength(s) emitted upon exciting waste water with light in the range 380-210 nm, and providing the appropriate ClO_2-dose based on the output of said measurement/assessment and the current ClO_2-demand.

23. A method according to any one of the preceding claims comprising ClO_2 providing means comprising flow controlling means adapted to provide a controlled flow of ClO_2 in water or a gas phase containing ClO_2, dosing means adapted to provide ClO_2 in a controlled dose/concentration, and feed-back means.

24. A method according to claim 23, wherein said ClO_2 providing means provide ClO_2 as a function of, or are proportional to one or more of:

(a) flow of waste water;

(b) level of estrogenic substance(s);

(c) ClO_2-demand; and/or

(d) feedback means.

25. A water treatment plant adapted to removing estrogenic substances according to any one of the preceding claims.

FIGURES

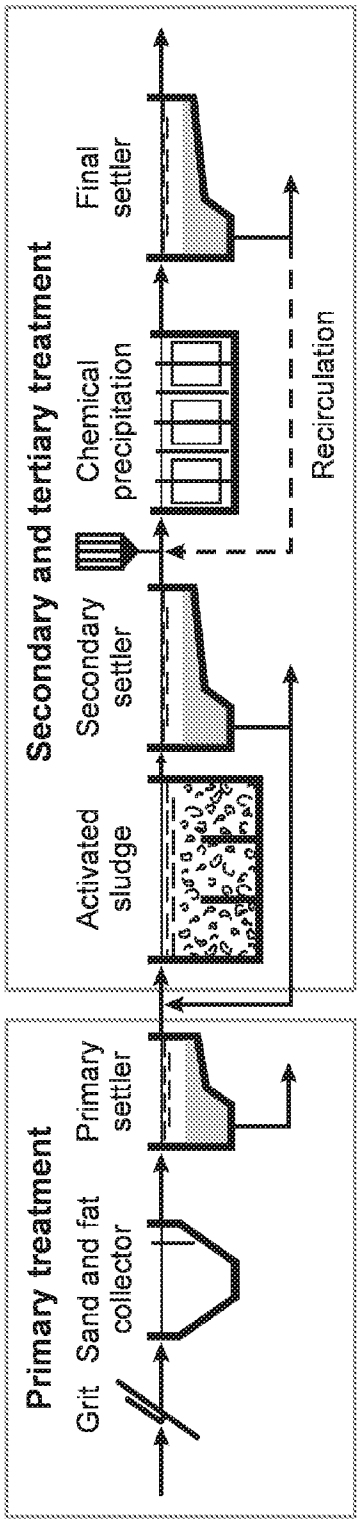

Figure 1

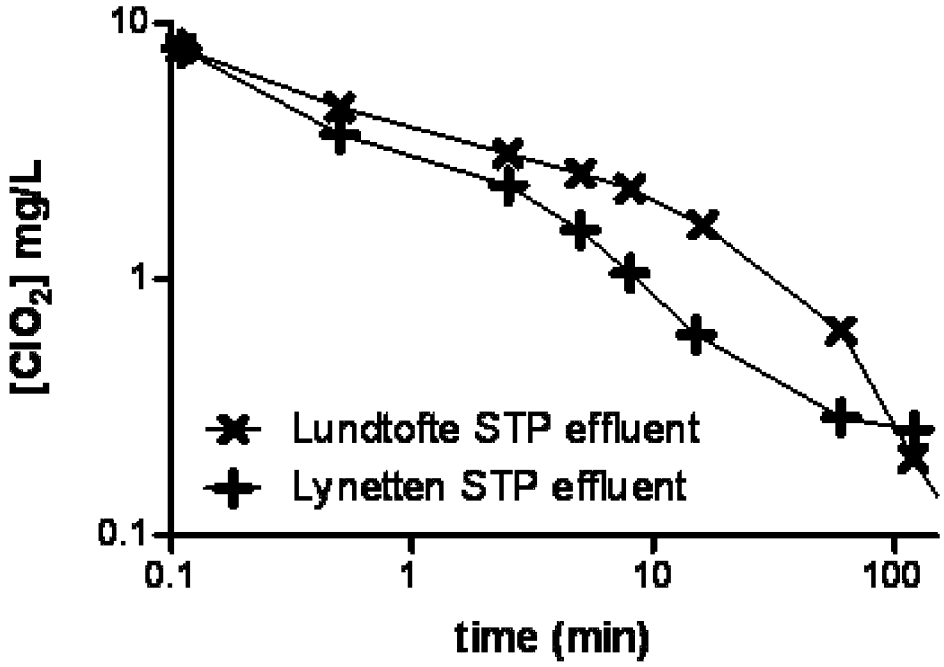
10
1
0.1
[ClO2] mg/L
Lundtofte STP effluent
Lynetten STP effluent
0.1
1
10
100
time (min)

Figure 2

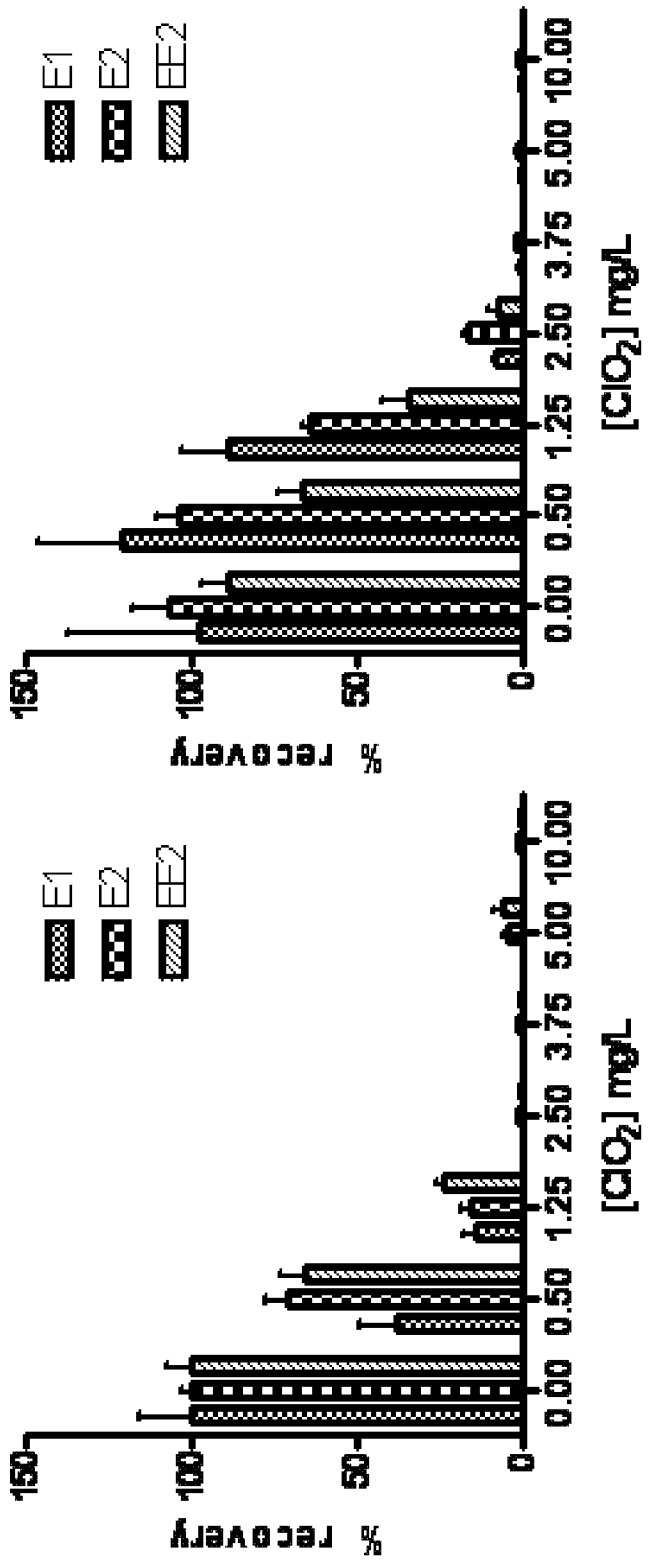
E1
E2
EE2
% recovery
150
100
50
0
0.00
0.50
1.25
2.50
3.75
5.00
10.00
[ClO2] mg/L
E1
E2
EE2
% recovery
150
100
50
0
0.00
0.50
1.25
2.50
3.75
5.00
10.00
[ClO2] mg/L

Figure 3

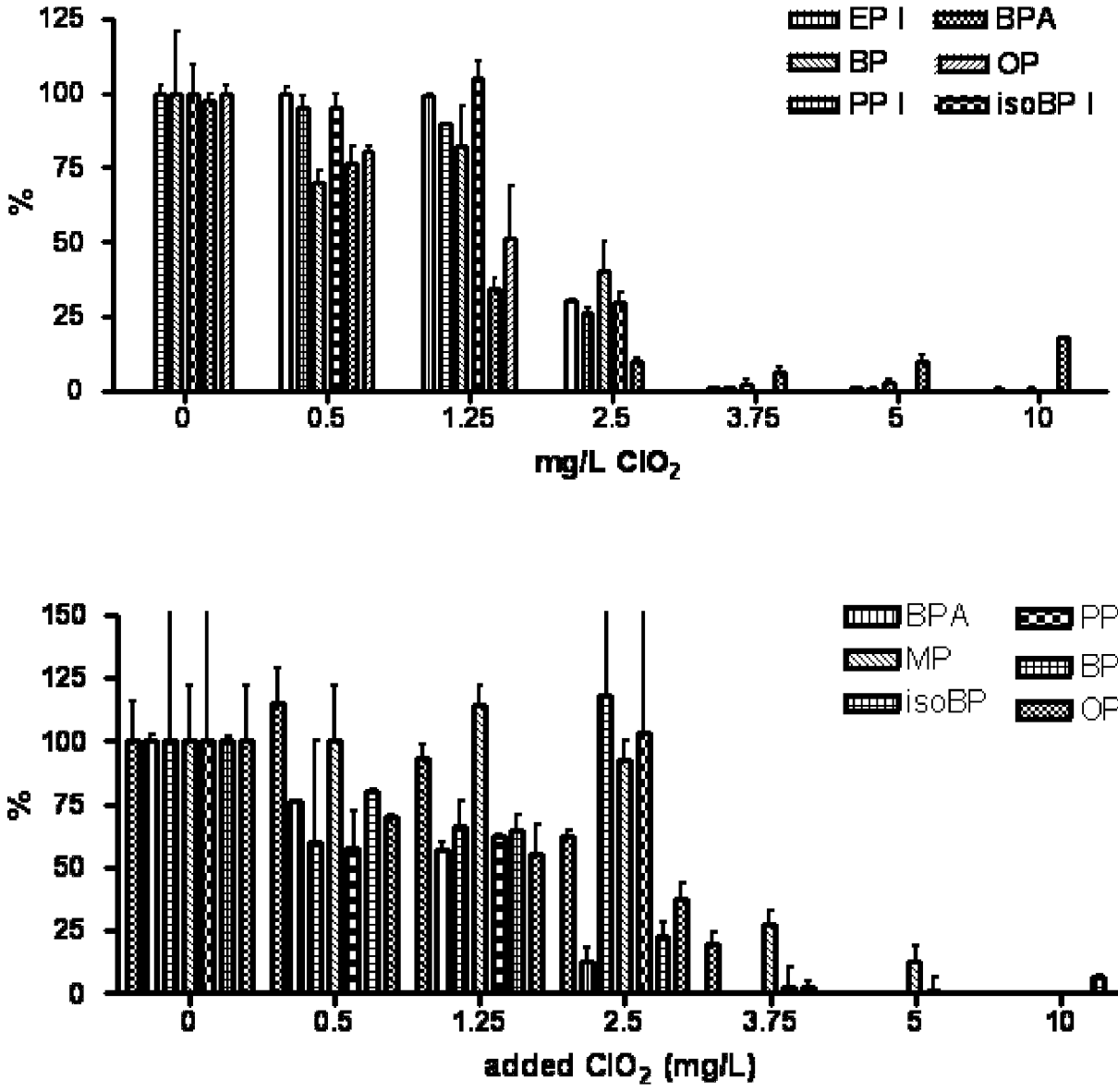
125
100
75
50
25
0
%
EP I
BPA
BP
OP
PP I
isoBP I
0
0.5
1.25
2.5
3.75
5
10
mg/L ClO2
150
125
100
75
50
25
0
%
BPA
PP
MP
BPA
isoBP
OP
0
0.5
1.25
2.5
3.75
5
10
added ClO2 (mg/L)

Figure 4

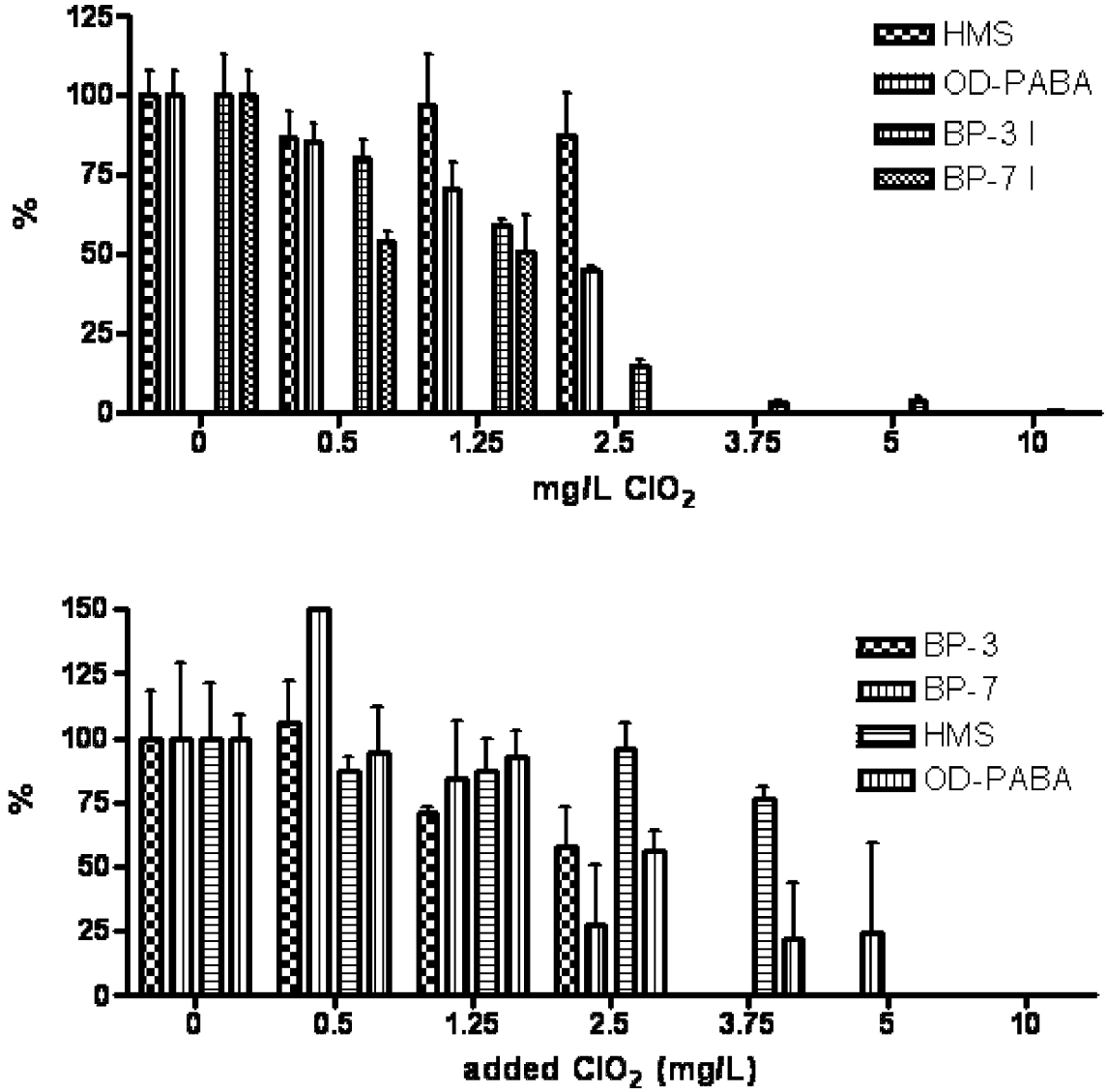
125
100
75
50
25
0
%
0
0.5
1.25
2.5
3.75
5
10
mg/L ClO2
HMS
OD-PABA
BP-3 I
BP-7 I
150
125
100
75
50
25
0
%
0
0.5
1.25
2.5
3.75
5
10
added ClO2 (mg/L)
BP-3
BP-7
HMS
OD-PABA

Figure 5

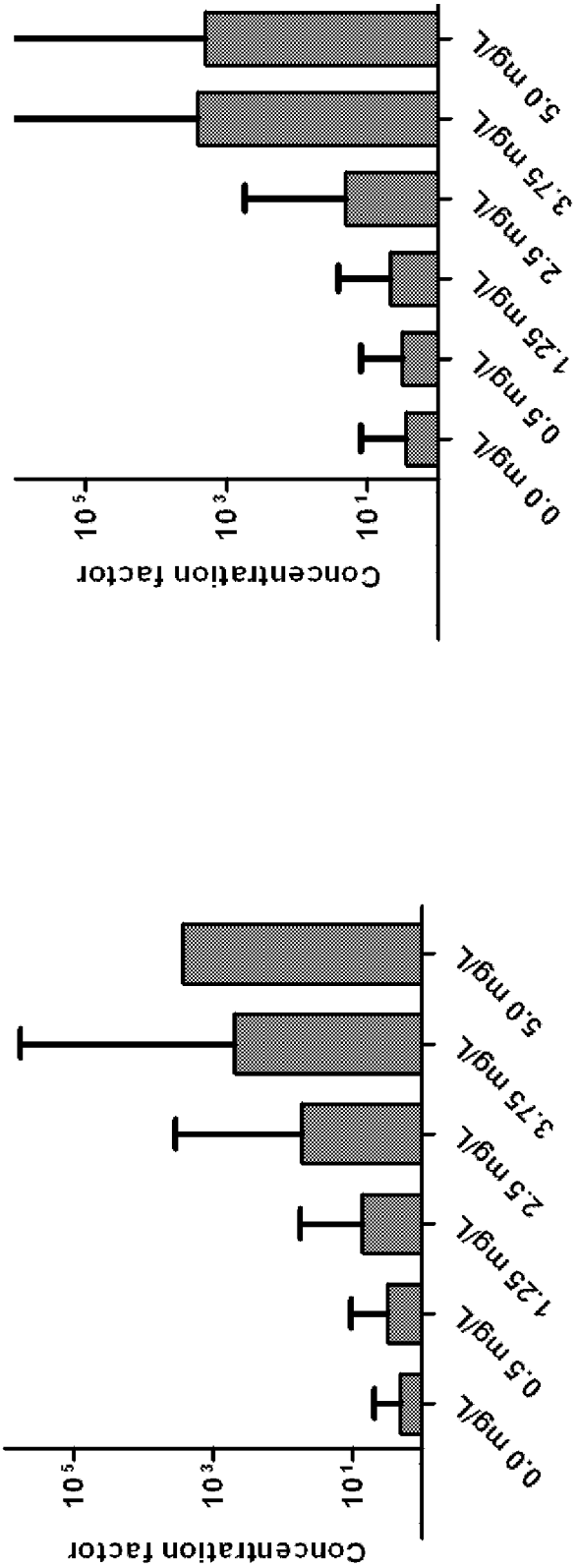
Concentration factor
10^5
10^3
10^1
0.0 mg/L
0.5 mg/L
1.25 mg/L
2.5 mg/L
3.75 mg/L
5.0 mg/L
Concentration factor
10^5
10^3
10^1
0.0 mg/L
0.5 mg/L
1.25 mg/L
2.5 mg/L
3.75 mg/L
5.0 mg/L

Figure 6

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2009/061208

A. CLASSIFICATION OF SUBJECT MATTER
INV. C02F1/76

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C02F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	ANDERSEN H.R., LUNDSBYE M., WEDEL H.V., ERIKSSON E., LEDIN A.: "Estrogenic personal care products in a greywater reuse system" WATER SCIENCE AND TECHNOLOGY, vol. 56, no. 12, 2007, pages 45-49, XP008100030 the whole document ----- -/--	1-15

[X] Further documents are listed in the continuation of Box C. [ ] See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
10 November 2009	20/11/2009

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Rozanska, Agnieszka

Form PCT/ISA/210 (second sheet) (April 2005)

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	LEE Y., ESCHER B.IL, VON GUNTEN U.: "Efficient removal of estrogenic activity during oxidative treatment of waters containing steroid estrogens" ENVIRONMENTAL SCIENCE AND TECHNOLOGY, [Online] vol. 42, no. 17, 14 February 2008 (2008-02-14), pages 6333-6339, XP002509549 Retrieved from the Internet: URL:http://pubs.acs.org/doi/abs/10.1021/es7023302> [retrieved on 2009-01-07] the whole document	1-15
A	GILBOA Y., FRIEDLER E.: "UV disinfection of RBC-treated light greywater effluent: kinetics, survival and regrowth of selected microorganisms" WATER RESEARCH, vol. 42, 4 October 2007 (2007-10-04), pages 1043-1050, XP002509550 the whole document	1-15
A	JEFFERSON B., PALMER A., JEFFREY P., STUETZ R., JUDD S.: "Grey water characterisation and its impact on the selection and operation of technologies for urban reuse" WATER SCIENCE AND TECHNOLOGY, vol. 50, no. 2, 2004, pages 157-164, XP002509553 the whole document	1-15
A	ALMEIDA M.C., BUTLER D., FRIEDLER E.: "At-source domestic water quality" URBAN WATER, no. 1, 1999, pages 49-55, XP002509554 the whole document	1-15
A	ERIKSSON E., AUFFARTH K., HENZE M., LEDIN A.: "Characteristics of grey water" URBAN WATER, no. 4, 2002, pages 85-104, XP002509555 the whole document	1-15
A	LENZ K., BECK V., FUERHACKER M.: "Behaviour of bisphenol A (BPA), 4-nonylphenol (4-NP) and 4-nonylphenol ethoxylates (4-NP1EO, 4-NP2EO) in oxidative water treatment process" WATER SCIENCE AND TECHNOLOGY, vol. 50, no. 5, 2004, pages 141-147, XP002554414 the whole document	1-25